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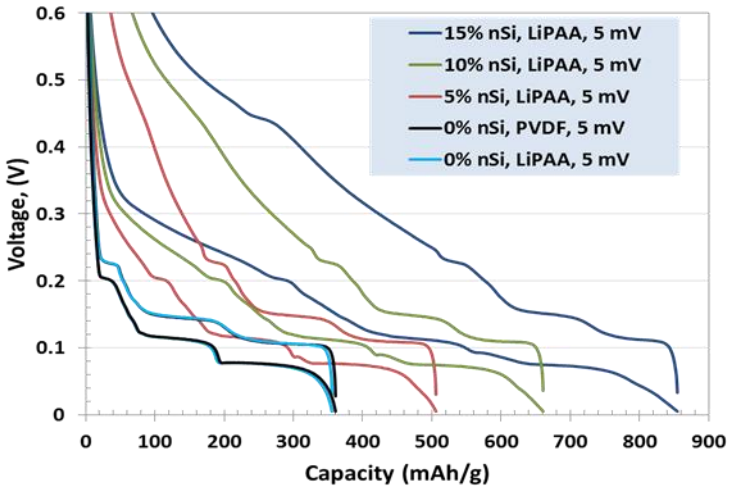
RESEARCH FACILITIES SUPPORT

Silicon Deep Dive



KYLE FENTON

U.S. DEPARTMENT OF ENERGY
VEHICLE TECHNOLOGIES OFFICE
2018 ANNUAL MERIT REVIEW

Project ID# BAT349

This presentation does not contain any proprietary, confidential, or otherwise restricted information

OVERVIEW

Timeline

- Start: October 1, 2015
  - Reset: October 1, 2017
- End: September 30, 2020
- Percent Complete: 55%

Budget

- Total project funding:
  - FY18 - $3600K
- Presentations: BAT349, BAT350, BAT351, BAT352, and BAT353

Barriers

- Development of PHEV and EV batteries that meet or exceed DOE and USABC goals
  - Cost, Performance, and Safety

Partners

- Sandia National Laboratories
- Pacific Northwest National Laboratory
- Oak Ridge National Laboratory
- National Renewable Energy Laboratory
- Lawrence Berkeley National Laboratory
- Argonne National Laboratory

RELEVANCE

- **Objectives: Stabilize the SEI - Stabilize the electrode**
- **Overall focus on insights into and advancement of silicon-based materials, electrodes, and cells.**
- **Advancements verified on life and performance of full cells using standardized testing protocols.**

Program Directly Addresses Cost and Performance Barriers and Quantifies Safety

- Elemental silicon can theoretically store >3500 mAh/g.
- Battery Performance and Cost (BatPaC) Model indicates a silicon based anode coupled with a high capacity cathode lithium-ion technology presents a pathway to less than $125/kWh$_{use}$
- BatPaC also used to relate pack level benefits to program goals.
- Benefits reach diminishing returns after **1000 mAh/cm^3** (electrode basis) for both cost and energy density.
- Silicon with <75 wt% graphite can achieve target.

MILESTONES AND ACTIVITIES

- **The program has more than twenty milestones related to the broad range of integrated activities listed below.**
- **Generally, milestones are either completed or on schedule.**

- Extensive electrochemical and analytical diagnostic studies.
- Facilities supporting program through a wide range of studies.
  - Battery Abuse Testing Laboratory (BATLab); Battery Manufacturing Facility (BMF); Cell Analysis, Modeling, and Prototyping (CAMP) Facility; Materials Engineering Research Facility (MERF); Post-Test Facility (PTF)
- Development and testing of coatings and additives designed to modify and stabilize the interface.
- Develop and analyze polymer binders designed to accommodate volume changes, increase conductivity, and improve adherence.
- Active material development.
  - Explore lithium inventory strategies.
  - Study alternative high-energy metals.

For reviewers, a detailed list of the milestones and progress is supplied in the reviewers only slides.

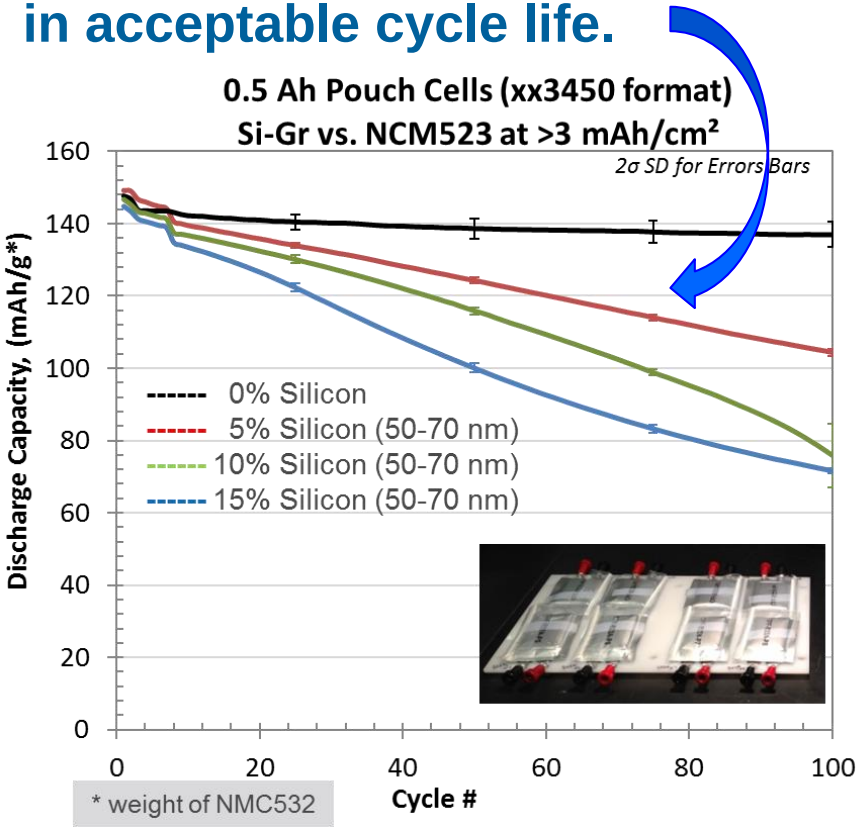
ANL CAMP FACILITY:

- A wide range of mixing equipment with various mixing actions that can work with small volumes of 10 mL up to 2 L of slurry, (ex. planetary mixer with high speed disperser); high precision electrode coater with two drying zones; a hot roll press, all which enables the fabrication of high quality electrodes.
- Semi-automated equipment to make xx3450 and xx6395 lithium-ion pouch cells with a typical capacity of 200 mAh to 4 Ah.
- Semi-automated equipment to make 18650 lithium-ion cells with a typical capacity of 1 to 3 Ah.
- Most equipment located in a dry room with an area of ~45 m² that is capable of maintaining <100 PPMv (-42°C dew point) with 6 people working and 750 SCFM of exhaust ventilation.
- Currently in the process of building a new dry room that will be ~135 m²

CHANGE DIRECTION OF ELECTRODE DESIGN

Previous efforts were focused on using low amounts of silicon (<15%), but with high levels of lithiation (~50 mV vs. Li^+/Li).

This approach has not resulted in acceptable cycle life.



BAT350

This year's effort is exploring the use of higher amounts of silicon (30-70%), but with lower levels of lithiation (>100 mV vs. Li^+/Li).

- **Will lessen degree of silicon particle expansion**
- **Incorporating other carbon materials (*e.g.*, hard carbon) instead of graphite because lower voltage plateau of graphite would not be utilized**
- **May enable other binder systems**

Electrode and testing standardization

Focus on processing and performance issues with materials choices for program

CHARACTERIZATION OF NEW SILICON MATERIAL FROM PARACLETE ENERGY

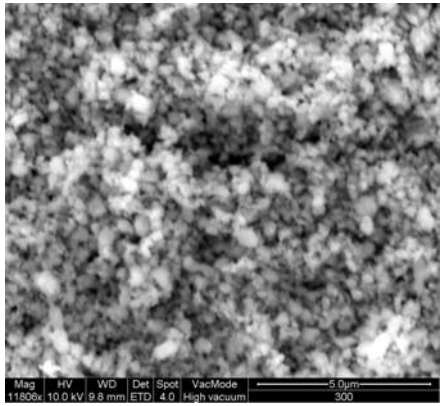
BAT351

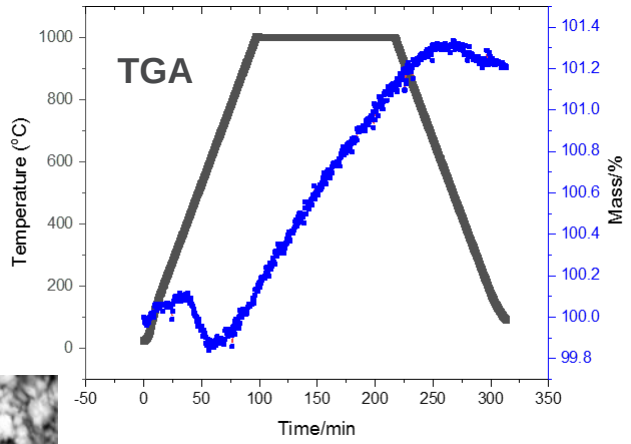
4 kg of Si/SiO (PE "4KD"Lot – F17-021-LS) was ordered and distributed to lab partners.

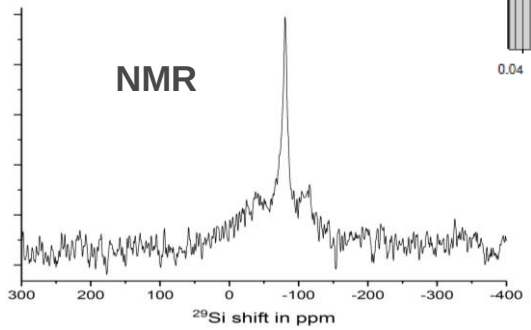
This 4 kg lot was analyzed and found to be comparable to the original 500 g lot used for initial evaluation

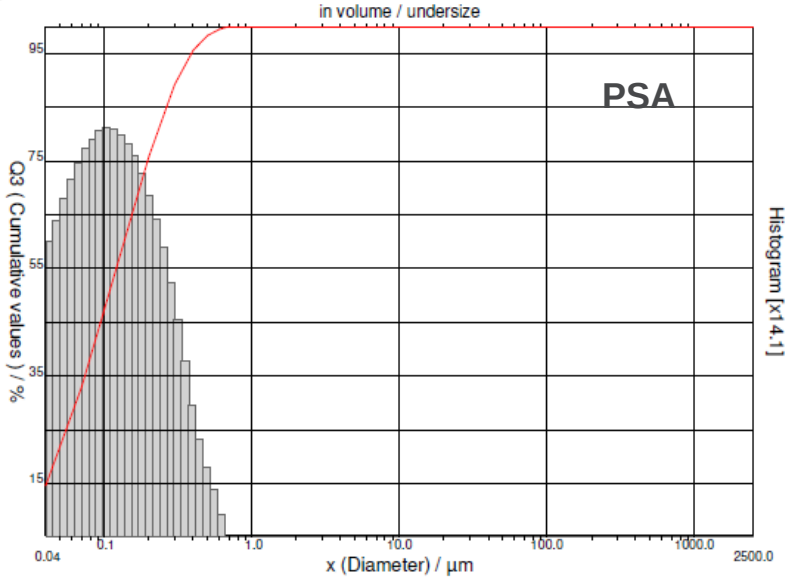
PARACLETE ENERGY

SEM









Sample 4KD will be used after the original 500g batch of D is used up

500g D lot was used in A-A012 and A-A013 in Electrode Library

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CHEMICAL ANALYSIS OF SILICON MATERIALS

A full panel ICP-MS study was performed to assess the amount of impurities in silicon materials from various sources. (Still working on finding a method to get accurate O_2 content)

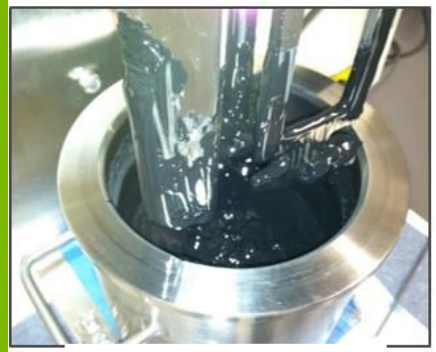
CAMP Sample No.	F17-005-LS-AR	NA-70-130 APS	NA-50-70 APS	HQ-80 APS	4KD
	Ground	Ground	Grown	Grown	Ground
ACL Sample No.	18-0013-01	18-0017-01	18-0017-02	18-0027-01	18-0039-01
Li	< 1.08	2.51	1.58	< 0.79	< 0.47
B	< 4.04	5.31	< 1.53	5.87	NA
Na	12.6	244	247	< 0.78	0.8
Mg	< 0.37	6.73	10.2	28.8	< 1.64
Al	< 0.63	159	16.3	1040	< 2.04
Si	NA	NA	NA	NA	NA
P	< 12.4	20.5	< 8.21	< 15.9	< 19.2
K	< 10.9	< 6.82	< 7.22	23.2	< 5.0
Ca	< 25.8	122	26.4	172	< 10.5
Ti	101	1621	0.84	146	0
V	< 0.04	4.02	< 0.03	128	< 0.03
Cr	1.52	< 0.29	< 0.31	58.5	2.50
Mn	0.34	3.73	< 0.05	73.1	0.33
Fe	< 7.03	32.3	< 5.34	4427	< 13.26
Co	0.86	3.43	12.6	13.1	3.70
Ni	1.07	5.80	< 0.08	64.9	1.27
Cu	23.8	11.6	7.62	99.7	2.7
Zn	11.8	4.58	2.47	10.8	0.8
Ga	< 0.01	0.09	< 0.01	2.94	< 0.02
Ge	< 0.05	1.87	< 0.05	2.18	< 0.27
As	< 0.16	1.35	< 0.17	6.38	< 0.18
Se	< 1.33	< 0.87	< 0.92	< 2.54	< 3.29
Rb	< 0.01	< 0.01	< 0.01	0.10	< 0.01
Sr	< 0.02	0.31	< 0.08	1.13	< 0.07
Y	91.3	74.8	< 0.04	0.65	126.0
Zr	1428	1103	0.17	11.5	2001
Nb	< 0.03	0.30	< 0.01	0.95	< 0.18
Mo	< 0.15	1.00	< 0.17	5.43	< 0.40

CAMP Sample No.	F17-005-LS-AR	NA-70-130 APS	NA-50-70 APS	HQ-80 APS	4KD
	Ground	Ground	Grown	Grown	Ground
ACL Sample No.	18-0013-01	18-0017-01	18-0017-02	18-0027-01	18-0039-01
Ru	< 0.01	< 0.02	< 0.01	< 0.01	< 0.01
Rh	< 0.01	< 0.02	< 0.01	< 0.01	< 0.01
Pd	< 0.02	< 0.02	< 0.02	< 0.22	< 0.02
Ag	< 3.90	65.5	< 0.02	3.86	< 0.27
Cd	0.76	0.77	< 0.03	< 0.04	0.70
Sn	< 0.04	0.35	0.08	0.92	< 0.16
Sb	< 0.02	0.25	< 0.04	0.88	< 0.05
Te	< 0.24	< 0.12	< 0.11	1.43	< 0.47
Cs	< 0.01	0.47	< 0.01	< 0.01	< 0.01
Ba	< 0.05	0.83	0.84	4.80	< 0.74
La	< 0.01	0.54	< 0.02	1.17	< 0.02
Ce	< 0.01	1.21	0.32	2.31	< 0.39
Pr	< 0.01	0.14	< 0.01	0.28	< 0.01
Nd	< 0.02	0.70	< 0.03	1.12	< 0.02
Sm	< 0.01	< 0.02	< 0.01	0.14	< 0.01
Eu	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Gd	< 0.01	0.06	< 0.01	2.52	< 0.01
Tb	< 0.01	< 0.00	< 0.01	0.03	< 0.01
Dy	< 0.01	< 0.02	< 0.01	0.18	< 0.02
Ho	< 0.01	0.06	< 0.01	0.04	< 0.01
Er	< 0.01	0.03	< 0.01	0.08	< 0.02
Tm	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Yb	< 0.01	< 0.01	< 0.01	0.05	< 0.01
Lu	< 0.01	< 0.01	< 0.01	< 0.01	< 0.02
Hf	50.2	39.3	< 0.01	0.34	50.9
Ta	< 0.01	0.17	< 0.01	0.20	< 0.76
W	< 3.53	< 3.73	< 1.35	< 1.66	< 1.32
Re	< 0.01	0.03	< 0.01	< 0.02	< 0.01
Ir	< 0.12	< 0.12	< 0.01	< 0.01	< 0.12
Pt	< 0.34	< 0.70	< 0.01	< 0.02	< 0.31
Au	< 0.06	< 0.14	< 0.05	< 0.06	< 0.09
Tl	< 0.01	< 0.01	< 0.01	< 0.01	< 0.06
Pb	0.62	1.86	0.76	1.53	0.16

Data Shown: PPM by weight

BATTERY MANUFACTURING FACILITY - ORNL

Pilot-Scale Electrode Processing and Pouch Cell Evaluation



Planetary Mixer (≤2 L)

Slot-Die Coating Line

Heated Calender (80,000 lb_f)

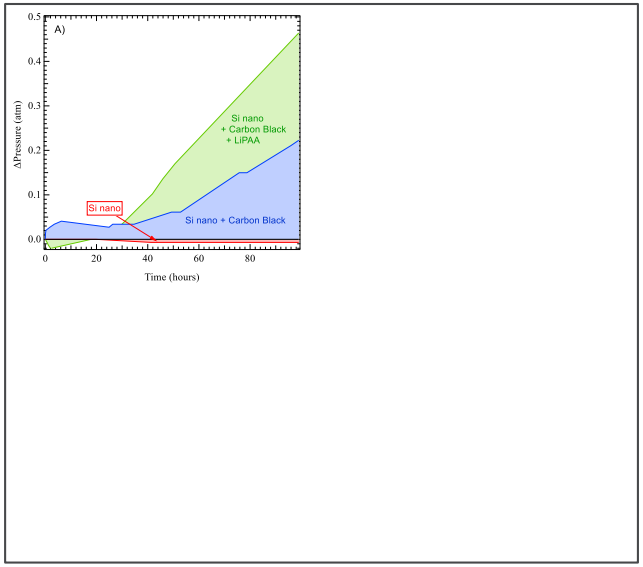
- All assembly steps from pouch forming to electrolyte filling and wetting.
- 1400 ft^2 (two 700 ft^2 compartments).
- Humidity <0.5% (-53°C dew point maintained).
- Pouch cell capacity: 50 mAh – 7 Ah.
- Single- and double-sided coating capability.
- Current weekly production rate from powder to pouch cells is 20-25 cells.

IDENTIFIED HOW PROCESSING CHANGES THE SURFACE CHEMISTRY OF SI AND HOW TO EXPLOIT

- Custom mixing vessel machined at ORNL allowed for monitoring of pressure and sampling of head space gasses

BAT345

Custom mill to capture evolved gas under realistic industrial conditions

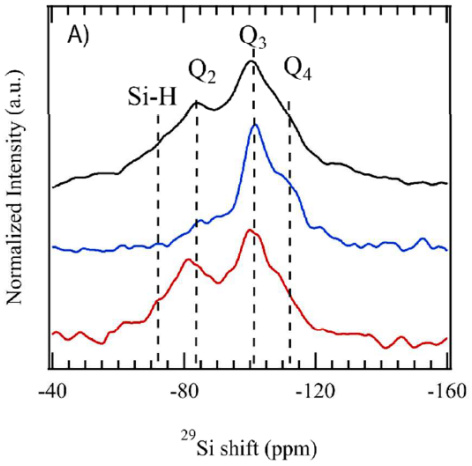


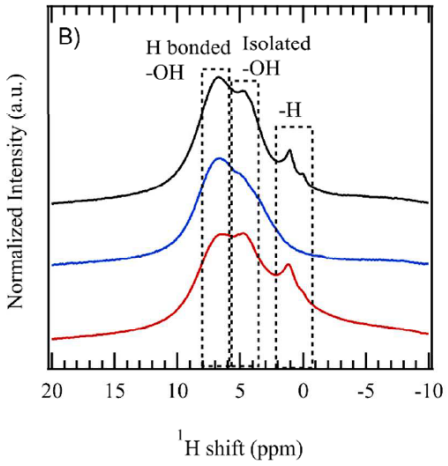
Monitor extent of gas produced during mixing

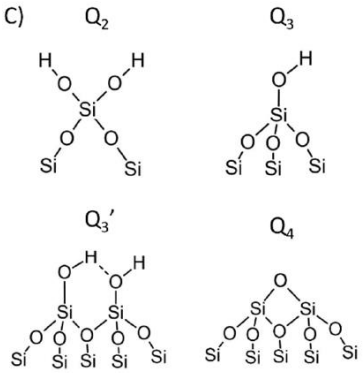
Silicon processing changes surface chemistry – implications for producibility and performance

Hays, K. A. et al. *J. Phys. Chem. C.* **2018,** *Under Review*.

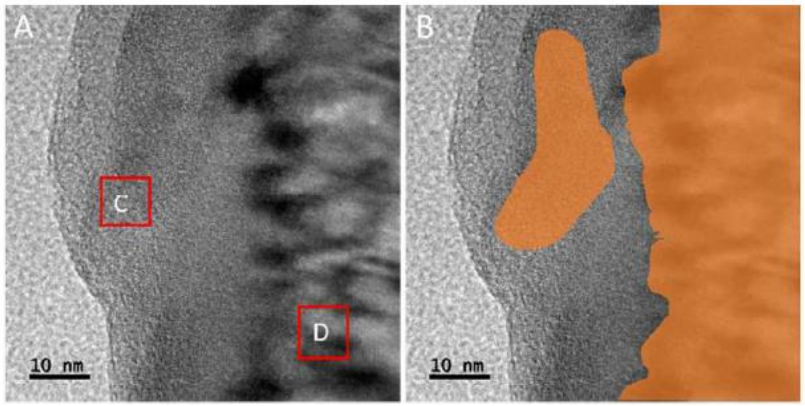
OBSERVE EXTENSIVE OXIDATION OF SI AND CHANGE OF SI SURFACE CHEMISTRY DEPENDING ON PROCESSING CONDITIONS AND TIME



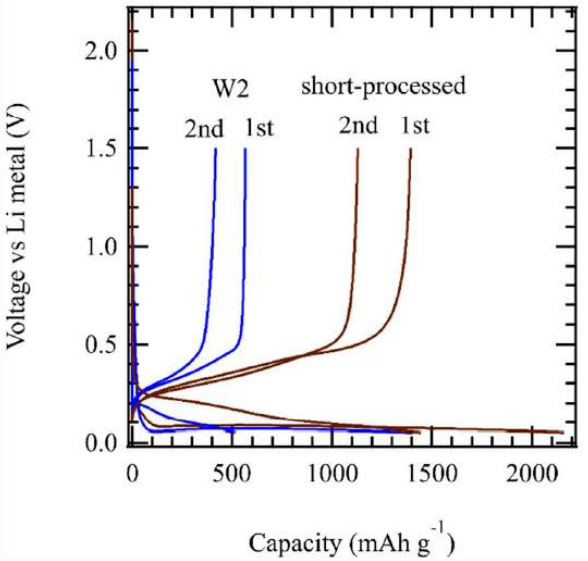




Milling introduces extensive changes to Si surface termination



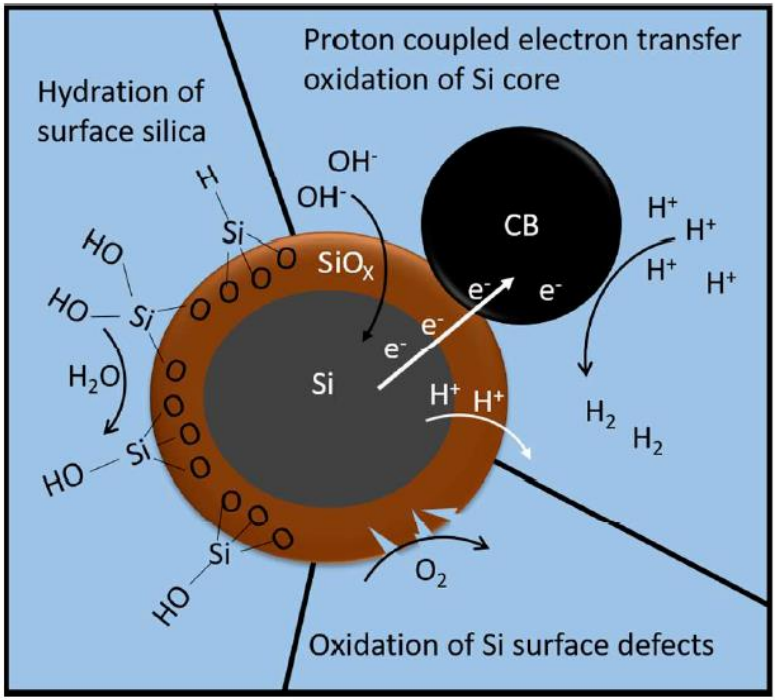
Loss of capacity due to formation of SiO_2 on surface



Hays, K. A. et al. *J. Phys. Chem. C.* **2018,** *Under Review*.

ADDITION OF CARBON BLACK INTO AQUEOUS BASED SILICON SLURRIES IS THE MAJOR CAUSE OF H_2 GAS AND SILICON CORROSION

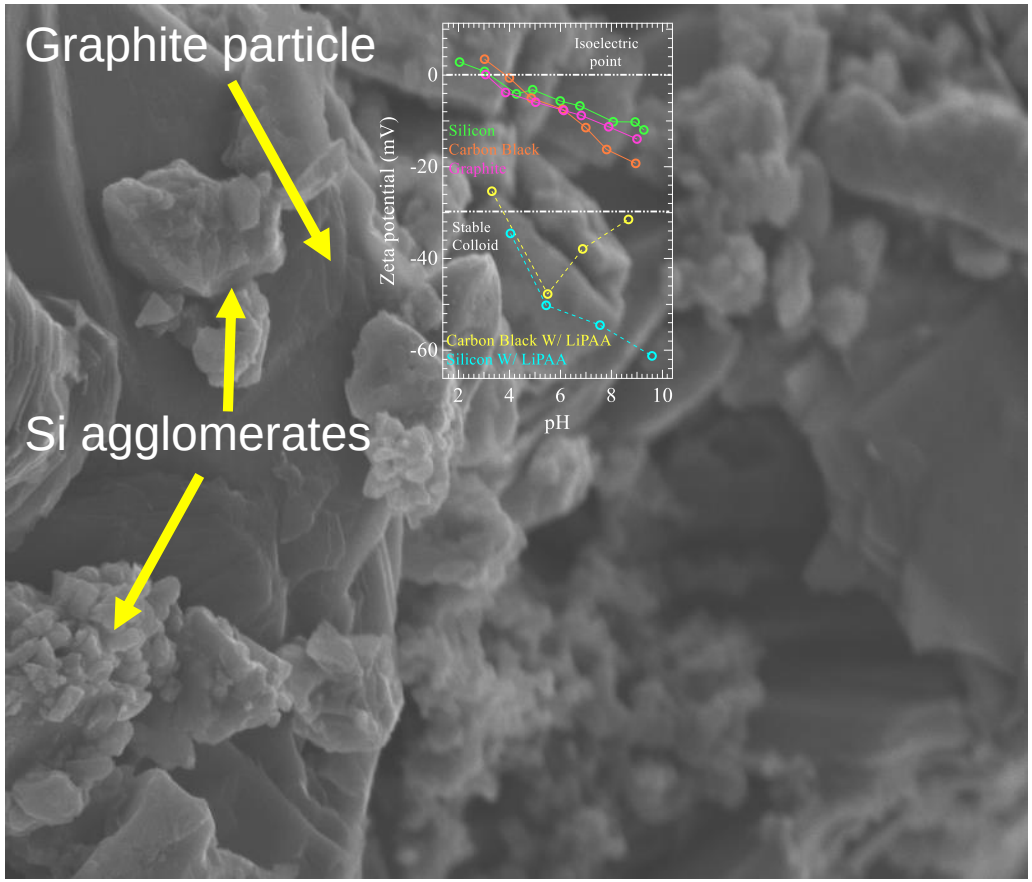
- Oxidation of Si by water only initiated in the presence of carbon black, forming significant amounts of H_2
- Oxidation also occurred at a faster time scale through consumption of atmospheric O_2 at surface defect sites on the Si particles, this also occurred in NMP solvent
- Additional gas build-up came from CO_2, which likely occurred due to LiPAA decomposition
- Long periods of mixing can lead to excessive Si oxidation, as verified by ^{29}Si MAS NMR



Hays, K. A. et al. *J. Phys. Chem. C.* **2018,** *Under Review*

SURFACE CHARGE OF SLURRY COMPONENTS IMPACTS PARTICLE AGGLOMERATION

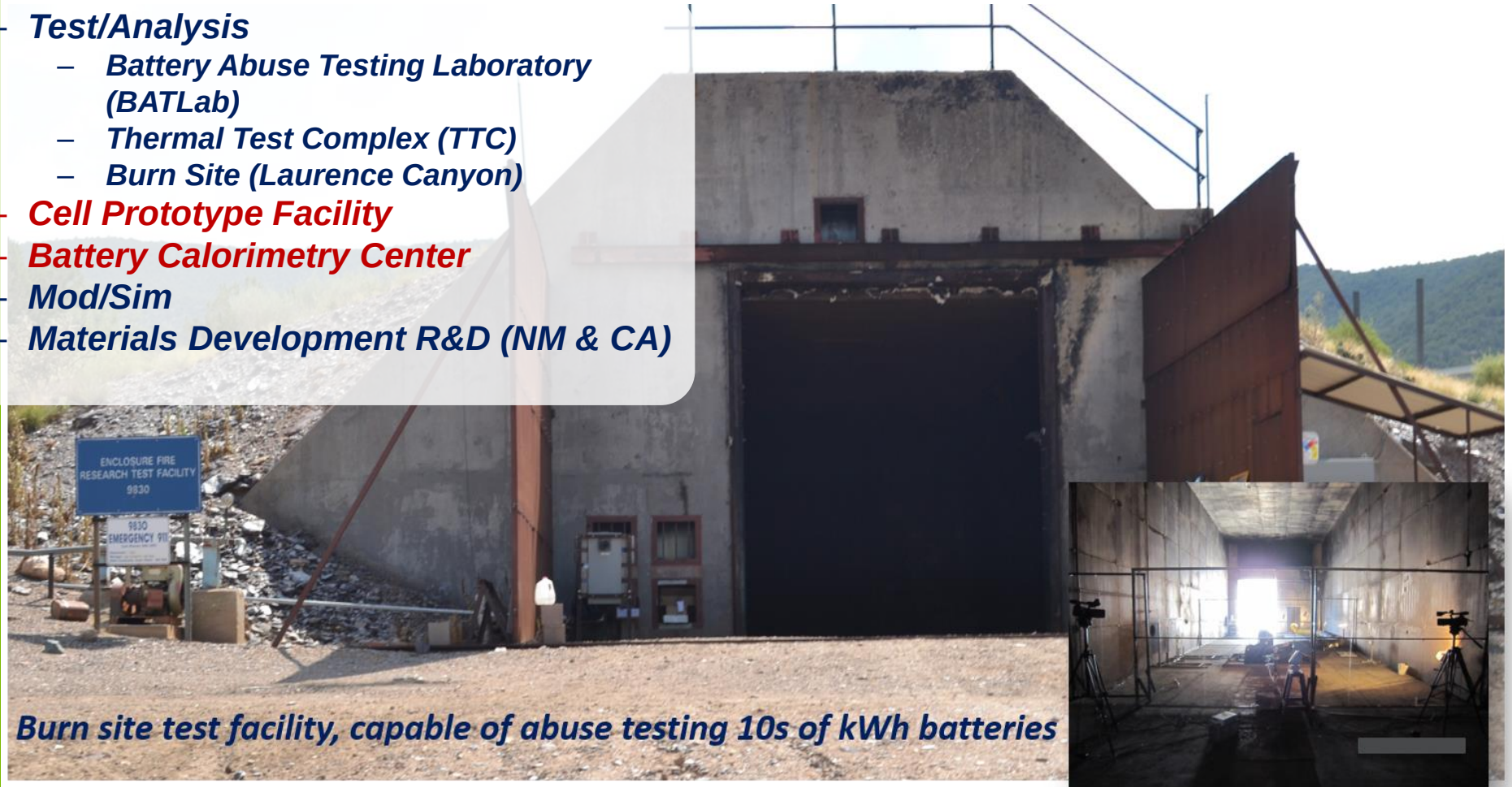
- Species with high surface charge form more stable dispersions, which minimize agglomeration in cast electrodes
- Zeta potential (ζ) of Si-graphite composite electrode materials verified on two different instruments at ORNL
- All components have low ζ in water, indicating lack of hydroxyl groups, which are sensitive to pH change
- Addition of LiPAA shifts ζ of Si and carbon black into a stable region
- Ideal pH for dispersion ~ 5.5



Zeta Potential – key parameter to predict stable slurry formulation

SNL BATTERY ABUSE TESTING LABORATORY (BATLAB)

- *Test/Analysis*
  - *Battery Abuse Testing Laboratory (BATLab)*
  - *Thermal Test Complex (TTC)*
  - *Burn Site (Laurence Canyon)*
- *Cell Prototype Facility*
- *Battery Calorimetry Center*
- *Mod/Sim*
- *Materials Development R&D (NM & CA)*

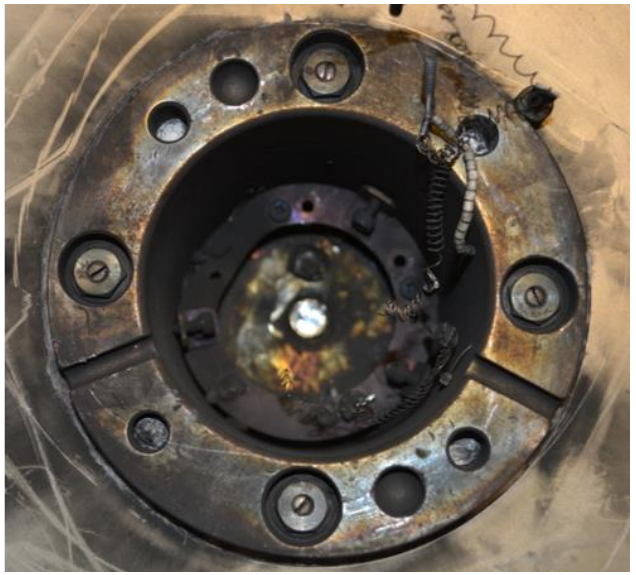


Burn site test facility, capable of abuse testing 10s of kWh batteries

ABUSE RESPONSE OF SILICON ANODES DURING ARC EVALUATION

Larger scale silicon cells exhibit significant response under abuse

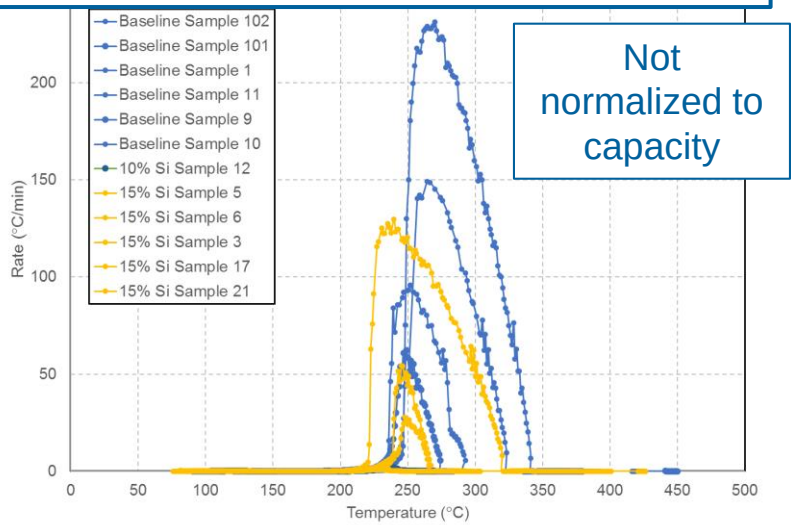
Complete rupture for entire ARC system seen with nano silicon electrodes at both 10 and 15% Si (both ARCs same result) – only a few instances of this occurring in SNL abuse testing



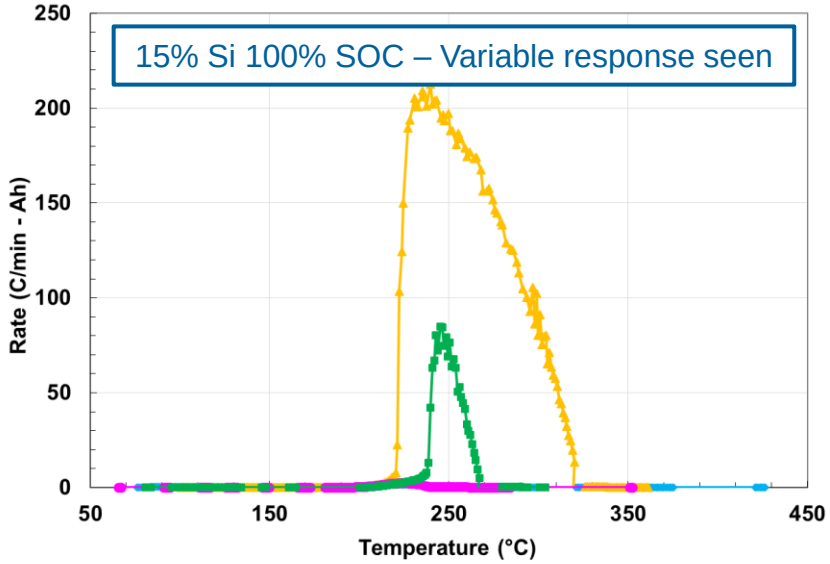
DPA analysis for cells show no indication of manufacturing defects. Results suggest energetic runaway is attributed to chemical decomposition.

CALORIMETRIC EVALUATIONS

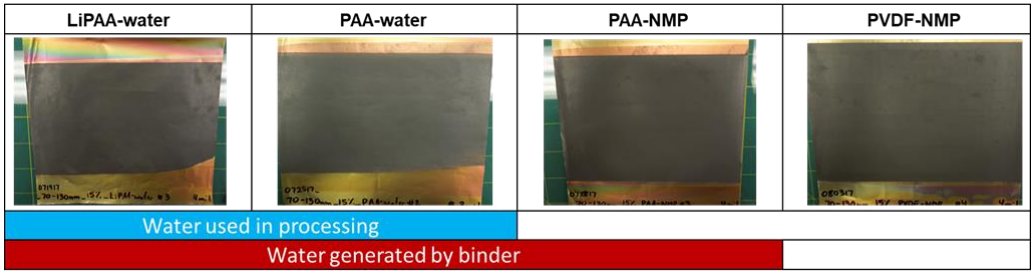
Small capacity cells – no control of response



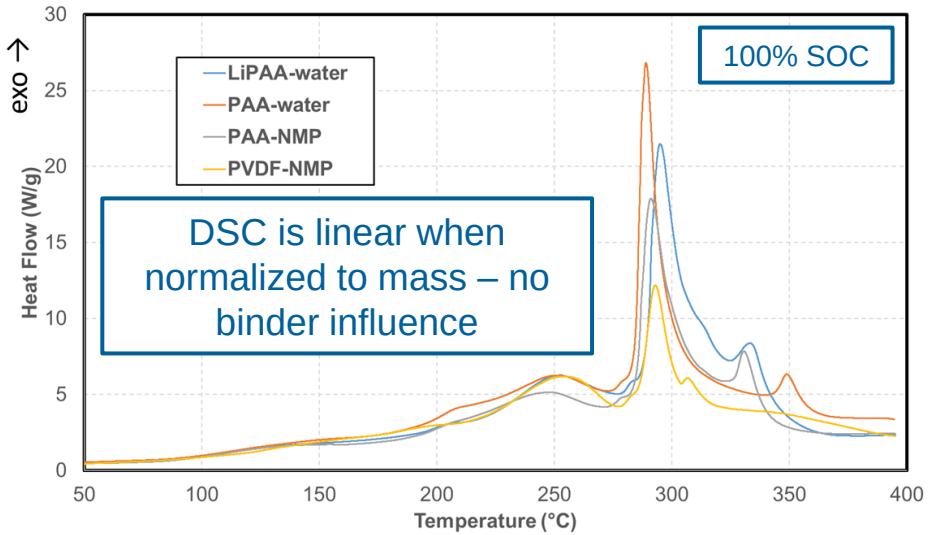
Not normalized to capacity



Investigation into binder role at electrode level



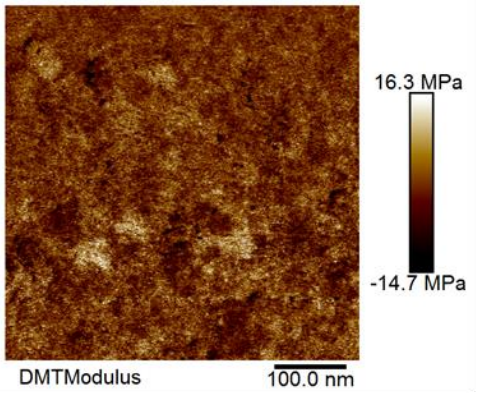
15% nSi electrodes



- Complex system that will require better control over surface reactivity for comparison – future work

BATTERY AND MATERIALS TESTING AND DIAGNOSTICS LEVERAGE FOR SILICON

- SNL Test Facility used for Tee and cell level testing
  - Different Temperature and conditions for all cells
- Safety for scale up to 50A-hr testing per chamber
- Diagnostics (EC-AFM, XPS, XRD, EC-TEM, Auget, TOF-SIMS) available at need



EC-AFM image of Si-substrate after electrochemical cycling and poise at lithiating potential, see talk BAT348

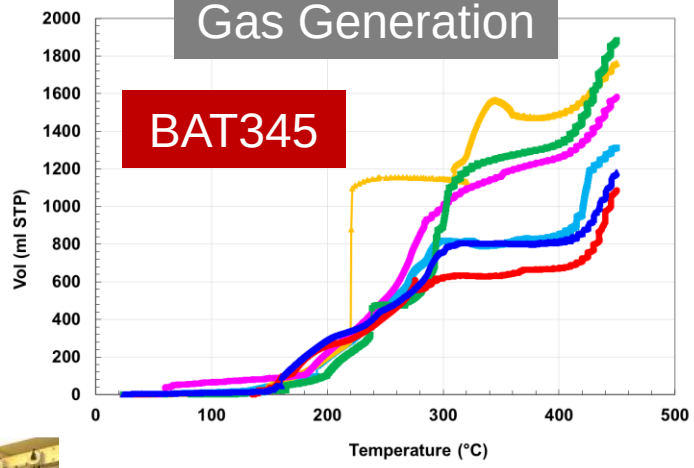
BAT348

SEI Interaction and performance

Battery aging facility; ~400 channels dedicated to lifetime monitoring of batteries under environmental conditioning

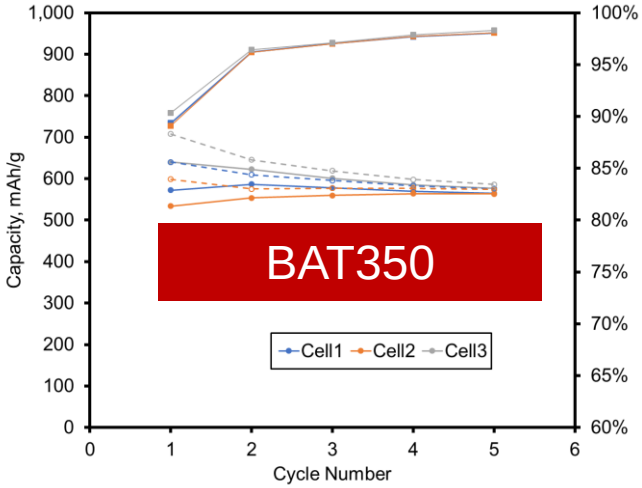
Gas Generation

BAT345



Performance

BAT350



MATERIALS ENGINEERING RESEARCH FACILITY

Advanced Battery Materials Process R&D and Scale Up

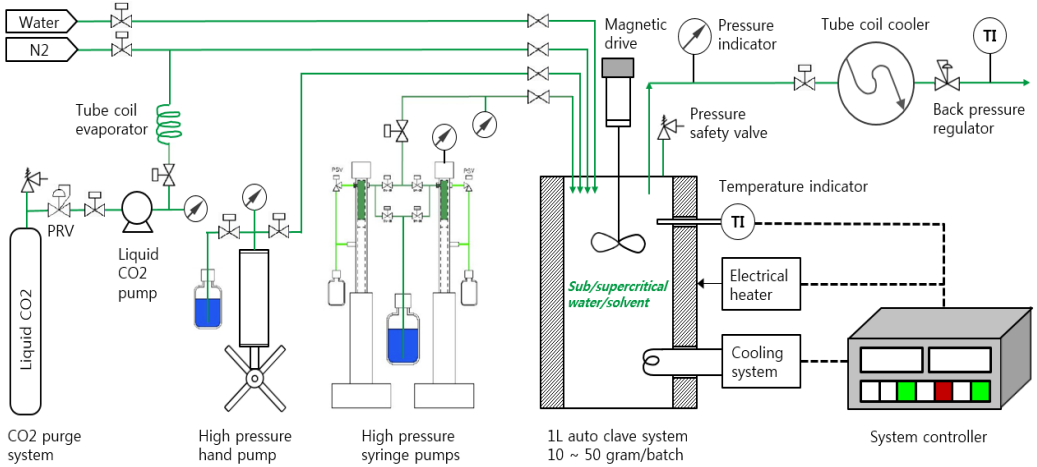
- Develop scalable manufacturing processes for new, advanced materials.
- Produce kilogram quantities of the material and make samples available for further research, industrial evaluation and prototyping.
- Develop analytical methods and quality control procedures. Investigate purity and impurity profile impact on performance to establish material specification.
- Evaluate emerging materials synthesis technologies to lower manufacturing cost while maintaining high quality of the material.

HYDRO/SOLVOTHERMAL SYNTHESIS AND SCALE-UP OF SILICON AND SILICON-CONTAINING NANOPARTICLES

Milestones

Date	Description	Status
Oct-17	Project start	Done
Nov-17	System basic design	
Dec-17	Basic design review	
Jan-18	PO of equipment and parts	
Apr-18	System installation start	On track
May-18	WCD/ESH preparation	
Jul-18	Mechanical completion	
Jul-18	System safety review	
Aug-18	Revision and modification	
Aug-18	Operation permission	
Sep-18	Si nanoparticle synthesis	
Oct-18	30 g delivery to collaborator	
Nov-18	Si/C composite synthesis	
Dec-18	100 g delivery to collaborator	

Schematic diagram of bench-scale hydro/solvothermal reactor system



- A new scalable Si synthesis process will be set up.
- Si nanoparticle size and morphology will be controlled and optimized by adjusting operation pressure, temperature and reaction medium.
- Si/C composite will be synthesized to increase the uniformity of Si and graphite in laminate film.

BAT345 – Si production

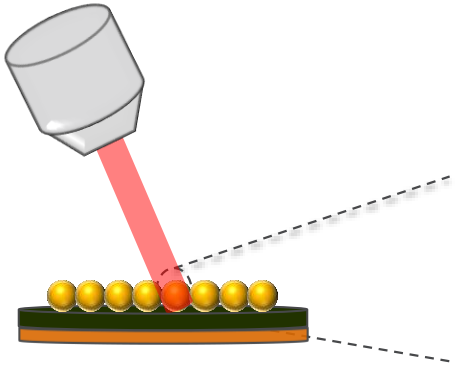
POST-TEST FACILITY AT ARGONNE SUPPORTS SI DEEP DIVE

- Post-test diagnostics of aged batteries can provide additional information regarding the cause of performance degradation, which, previously, could be only inferred
- Combine microscopy, spectroscopy and chromatography in a controlled-atmosphere glove box to the greatest extent possible
  - FT-IR spectroscopy
  - Raman spectroscopy
  - Optical and scanning-electron microscopy
  - Electrochemical impedance spectroscopy
  - X-ray photoelectron spectroscopy
  - High Pressure Liquid Chromatography/Gel Permeation Chromatography
  - TGA-GC/MS
  - Half-cell fabrication and test equipment

- Use capabilities to characterize pristine and aged Si-based electrode materials and Li-Si phases

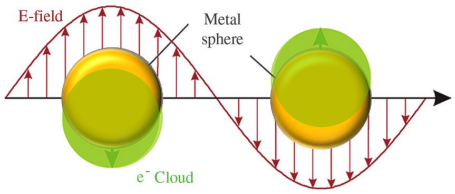
SURFACE ENHANCED RAMAN SPECTROSCOPY (SERS)

Pristine Si anodes



Au NPs deposited over the sample to be enhanced

LSPR (localized surface plasmon resonance) is involved.



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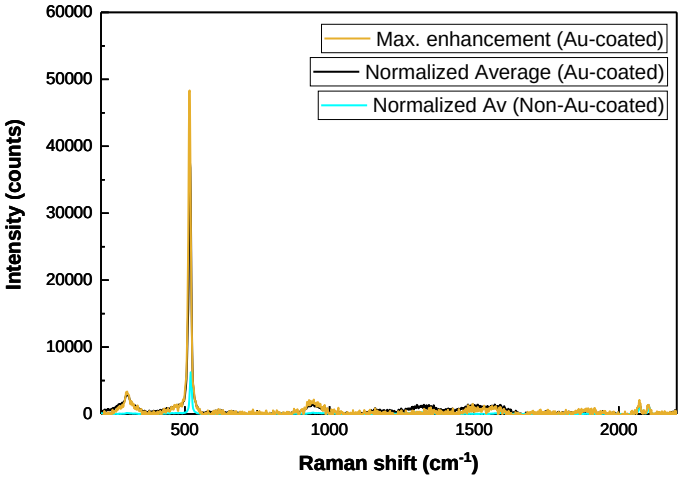
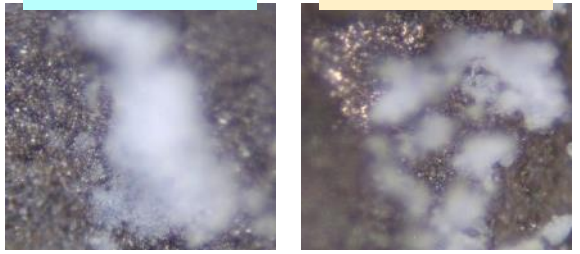
Raman intensity coming from molecules located in the vicinity of Au NPs excited by visible light can be strongly increased.



Average Raman enhancement factor = 5.3

Maximum Raman enhancement factor = 7.75

(Non-coated) (Au-coated)



$K_4[Fe(CN)_6]$ as reference (v_{CN} = 2074, 2105 cm^{-1})

CAMP electrodes (LN3107-71-1) :

- **70.7 wt. % NanoAmor Si (70-130 nm)**
- **9.4 wt. % Timcal C-45**
- **19.9 wt.% LiPAA (LiOH titrate)**

Post test capability used to probe behavior of silicon anode materials – advance understanding for both particulate and model systems

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RESPONSES TO PREVIOUS YEAR REVIEWERS' COMMENTS

Last year two poster presentations covered all the project. The two posters were each reviewed by eight reviewers. We thank the reviewers for their thoughtful comments. Selected excerpts are given below.

- Many of the reviewers' comments were generally positive.
  - "applauded the excellent, thorough approach"
  - "very ambitious program to assess advantages, disadvantages and solutions for Si anode materials"
  - "very nice intra-laboratory coordination"
- One reviewer thought we could further enhance the program by bringing in experts in mechanical stresses. We conduct limited mechanical measurements and have relied on literature to establish a stable particle size, but in general we agree more in-depth studies could improve the program.
- One reviewer suggested that our commitment to openness limits our ability to examine proprietary materials. We agree totally and recognize the limitation. However, we consider that the work we are doing is addressing the fundamental issues with silicon materials and will benefit the entire community.

REMAINING CHALLENGES AND BARRIERS

- Several key challenges remain that limit integration of silicon into graphitic negative electrodes, mostly related to the large crystallographic expansion of silicon (>300%) upon lithiation.
  - SEI stability issues, which affect cycling efficiency.
  - Electrode stability issues that include particle isolation, accommodating volume changes, and adherence.

COLLABORATION AND COORDINATION WITH OTHER INSTITUTIONS

- Six National Laboratories have teamed to form this integrated effort focused on gaining insights into and advancement of silicon-based materials, electrodes, and cells.
- This effort has strong interactions with the Silicon Electrolyte Interface Stabilization (SEI-Sta) project (BAT344, BAT345, BAT346, BAT347, and BAT348).
- Paraclete Energy is suppling baseline silicon materials.

CONTRIBUTORS AND ACKNOWLEDGMENT

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- Post-Test Facility (PTF)
- Materials Engineering Research Facility (MERF)
- Cell Analysis, Modeling, and Prototyping (CAMP)
- Battery Manufacturing Facility (BMF)
- Battery Abuse Testing Laboratory (BATLab)

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